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Polymer Filler Aging and Failure Studied by Lateral Force Microscopy

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1.1 Introduction

In the present work, we study, *via* force microscopy, the basic physical interactions of a single bead of silica filler with a PDMS matrix both before and after exposure to gamma radiation. Our goal was to confirm our results from last year, and to explore force microscopy as a means of obtaining particle-scale polymer/filler interactions suitable for use as empirical inputs to a computational model consisting of an ensemble of silica beads embedded in a PDMS matrix. Through careful calibration of a conventional atomic force microscope, we obtained both normal and lateral force data that was fitted to yield adhesion, surface shear modulus, and friction of a 1 μm silica bead in contact with PDMS layers of various thickness. Comparison of these terms before and after gamma exposure indicated that initially, radiation exposure lead to softening of the PDMS, but eventually resulted in stiffening. Simultaneously, adhesion between the polymer and silica decreased. This could indicate a serious failure path for filled PDMS exposed to radiation, whereby stiffening of the bulk polymer leads to loss of compressive elastic behavior, while a decrease in polymer filler adhesion results in an increased likelihood of stress failure under load.

In addition to further testing of radiation damaged polymers, we also performed FEA modeling of silica beads in a silicone matrix using the shear modulus and adhesion values isolated from the force microscopy experiments as model inputs. The resulting simulation indicated that as a polymer stiffens due to impinging radiation, it also undergoes weakening of adhesion to the filler. The implication is that radiation induces a compound failure mode in filled polymer systems.

1.2 Method

The adhesion and force interactions between a single bead of a spherical silica particle and cast and crosslinked M97 silicone were measured by lateral- and normal- Atomic Force Microscopy methods. Samples were studied as a function of radiation dosage and thickness. All experimental methods are available in a previously submitted report. [1].

1.3 Results and Discussion

Consistent with our prior report, exposure of M97 to a gamma radiation flux resulted in a decrease in the adhesive force between the silicone and a silica microprobe. As with our prior results, the force distribution narrowed with continuing radiation exposure. We speculate that the narrowing of the force distribution is due to a decrease in the number of adhesive molecular interactions with the silica bead as the polymer is continuously damaged by prolonged radiation exposure.

As we reported last year, Figures 1 and 2 show the results of radiation exposure on film surface adhesion and shear strength, respectively. Up to about 0.4 Mrad, adhesion force steadily drops then reaches a steady value. In nearly reciprocal fashion to the adhesion

measurements, the computed value of film surface shear strength increases with radiation dose over approximately the same interval as adhesion decreases. Taken together, these results indicate an overall stiffening of the film as a function of radiation exposure. In an earlier study of a silica filled M97 composite, radiation exposure in air was determined to induce increased crosslink density in the bulk polymer, while decreasing crosslink density in the near filler region [2]. This was interpreted as being due to the disruption of hydrogen bonding interactions between the polymer and the silica surface. Such a decrease in surface interactions can be considered as a loss of adhesion, in agreement with our results. However, as our experiments did not involve radiation exposure while the polymer and silica surface were in contact, the results imply that the decrease in adhesion originates with damage to the polymer alone, as opposed to radiolysis of the interface or interphase.

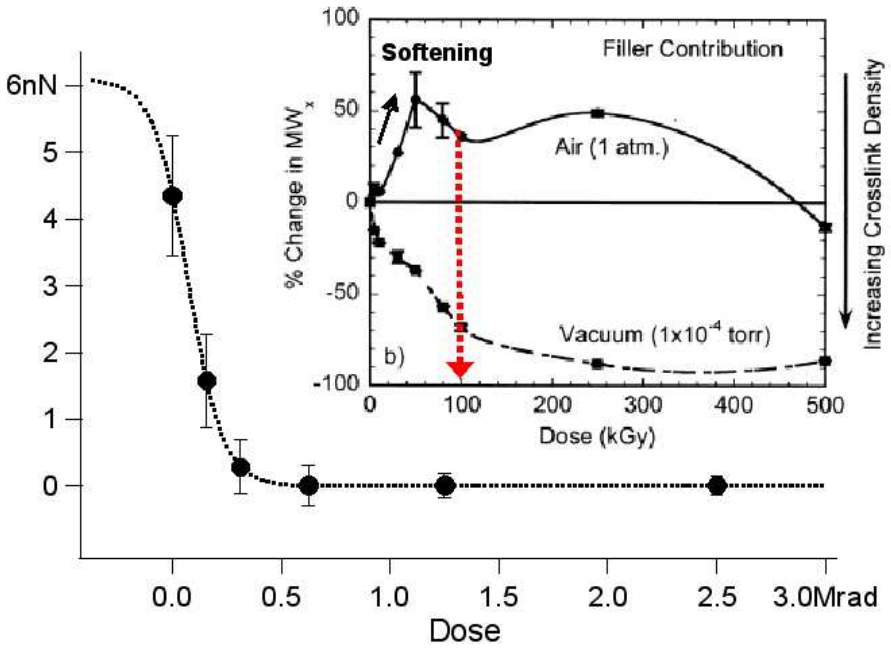

Figure 1. Adhesion force maxima as a function of radiation dose for silica filler particles and spin-coated M97 polymer films (data above 2.5 Mrad not shown). The dotted line indicates a sigmoidal fit to the data, displaying an upper saturation value of ~ 6nN, and a lower value of ~6.5 pN. The inset shows an earlier result from [2] that indicated a softening of bulk M9787 polymer-silica composite material and implicated the silica-polymer interface in the softening. The red dotted line in the inset indicates the maximum dose level of the nanoscale force measurements.

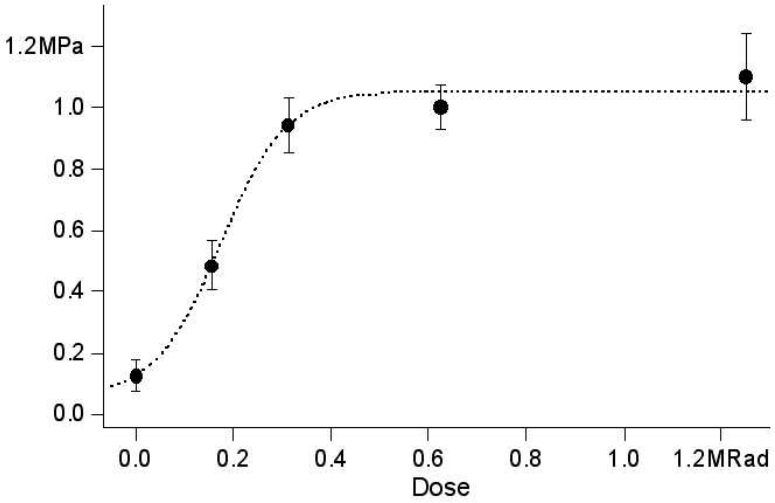

Figure 2. Shear strength as a function of radiation dose, as determined by lateral force microscopy

The foregoing values of shear modulus were used as inputs to a 2-D finite element analysis (FEA) model of silica beads embedded in a silicone matrix and subject to a compressive stress. The model was created in COMSOL [3] using the MEM package with plane strain and film damping. Material parameters (e.g. Poisson's ratio, thermal conductivity, expansion coefficient, etc.) were selected from within the COMSOL materials properties library. A variety of compressive tensor types was available, but based on the material system both isotropic and hyperelastic (neo-hookian) were chosen for comparison. The resulting difference between these two approaches was insignificant. A compressive force of 20 nN was applied. The value was chosen to be comparable to that estimated for a polymer part in service. The bounds of the configuration were 10 μm x 10 μm.

As seen in Figure 3, the accumulation of stress occured near the outer boundaries of the particles with respect to the geometrical center of the model configuration. What is most significant, however, is that the maximum stress levels at these points exceeded the measured adhesion after the completion of radiation exposure. Thus, the implication for failure of a rad exposed polymer is two-fold. First, radiation induces stiffening of the polymer, thus reducing compliance and increasing the liklihood of cracking. Second, the loss of adhesion increases the chances of delamination from the filler under stress, thus weakening the material by diminshing the reinforcing behavior of the filler. A more complete model will explicitly consider the measured adhesion and shear modulus to directly show the effects of radiation on the stress behavior of the filled polymer near the filler interface.

1.4 Conclusion.

Two potential failure routes in filled polymers exposed to stockpile relevant radiation fluxes have been discerned by using lateral- and normal- AFM. A filled silicone exposed to radiation will undergo simultaneous loss of compliance as well as a reduction in the polymer-filler interfacial adhesion. A comparison of the measured quantities after radiation exposure to a finite element model indicates that the loss of adhesion is sufficient to cause delamination at compressive stresses within the scope of systems. Our

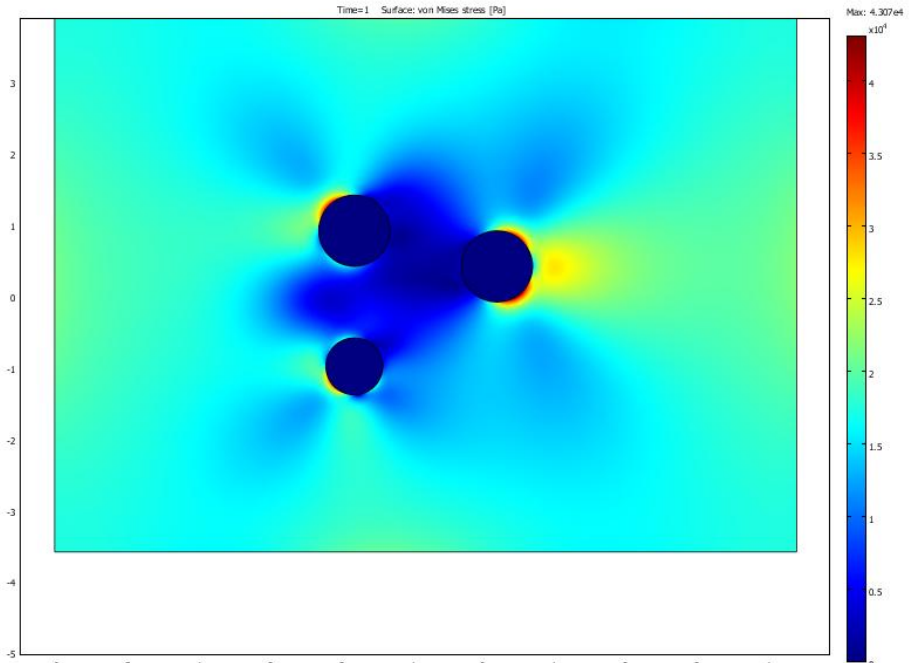

Figure 3. 2-D FEA solution for compression of a sample of silica beads embedded in a silicone matrix.

results also indicate that the effects of radiolysis on the interaction between filler and polymer originate from damage of the polymer alone, as opposed to damage to an interphase of the polymer and filler.

1.5 References

[1] LLNL ESC Annual Report, 2007
[2] Chien, A.; Maxwell, R.; Chambers, D.; Balazs, B.; LeMay, J., Characterization of radiation-induced aging in silica-reinforced polysiloxane composites. *Radiation Physics and Chemistry* **2000,** 59, (5-6), 493-500.
[3] COMSOL Multiphysics, Version 3.3a, 2007, COMSOL AB, Stockholm